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Composition dependent frequency upconversion of Er^{3+}/Yb^{3+}-codoped lead chloride tellurite glasses

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Abstract

The green and red upconversion luminescence of Er^{3+} in lead chloride tellurite glasses excited at 980 nm is investigated. Three intense emission bands centered at 530, 545, and 658 nm corresponding to the transitions $^4S_{3/2}\rightarrow{}^4I_{15/2}$, $^2H_{11/2}\rightarrow{}^4I_{15/2}$ and $^4F_{9/2}\rightarrow{}^4I_{15/2}$, respectively, were simultaneously observed at room temperature. With increasing $PbCl_2$ content, the intensity of green (530 nm) emissions increase slightly, while the green (545 nm) and red (658 nm) emissions increase significantly. The results indicate that $PbCl_2$ has more influence on the green (545 nm) and red (658 nm) emissions than the green (530 nm) emission. The dependence of upconversion intensities on excitation power and possible upconversion mechanisms are discussed and evaluated.

Keywords: Lead chloride tellurite glasses; Frequency upconversion; Fluorescence; Rare earth

1. Introduction

The development of diode-laser pumped upconversion lasers is a promising concept toward all solid-state visible wavelength lasers [1]. The main interest in visible lasers arises from wide range of applications in areas such as color display, optical data storage, optoelectronics, medical diagnostics, sensor, and undersea optical communication [2–6]. Upconversion lasers have realized on various transitions in erbium, thulium, neodymium and praseodymium. One of the most promising candidates for a green upconversion laser is $^4S_{3/2}\rightarrow{}^4I_{15/2}$ transition in trivalent erbium [7–9]. The choice of the host material is very important for Er^{3+} ions obtaining highly efficient upconversion signal, since glass host with low phonon energy can reduce the non-radiative loss due to the mutiphonon relaxation (MPR) and thus achieves strong upconversion luminescence [10]. Though fluoride glasses have been extensively studied due to low phonon energies, oxide glasses are more appropriate for practical applications due to their high chemical durability and thermal stability. Among oxide glasses, tellurite glasses have been intensively investigated because of their special properties such as the large resistance against devitrification, the possibility to incorporate a large amount rare-earth dopants, high refractive index and relative low phonon energy [11–13]. The low maximum phonon energy and high refractive index yield low non-radiative decay rates and high radiative emission rates for the energy levels of rare-earths upconversion luminescence has been reported in Er^{3+}-doped tellurite glasses [8], but the upconversion luminescence is weak. Efforts to enhance upconversion luminescence of Er^{3+}-doped tellurite glasses are still attracting attention [14].

As is known, glasses based on mixed oxide-fluoride systems combine the good optical properties of fluoride glasses (a broad range of optical transmittance and low optical losses) with the better chemical and thermal stability of oxide glasses [6,15]. So it is expected that the mixed glasses including tellurite and chloride should bring together the interesting properties of the two systems. Several investigations have focused on structural studies of chloride tellurite glasses recently [16–18]. However, little attention has been paid to the study of upconversion luminescence of Er^{3+} in these glasses. In this paper, we investigate the dependence of $PbCl_2$ on

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frequency upconversion of Er^{3+}/Yb^{3+}-codoped lead chloride tellurite glasses under 980 nm excitation. The results demonstrate that they can act as suitable materials for practical upconversion applications.

2. Experimental

The glasses used in this work were synthesized by a conventional melting and quenching method. The starting materials are reagent grade TeO_2, $PbCl_2$, Yb_2O_3 and Er_2O_3. The composition (mol%) of the prepared glasses are $(100-x)TeO_2$–$xPbCl_2$–$2Yb_2O_3$–$0.5Er_2O_3$ (TPCx), where $x = 10, 20, 30, 40, 50$. About 50 g batches of starting materials were fully mixed and then melted between 700°C and 750°C in covered platinum crucibles in a SiC Globar furnace with an N_2 atmosphere. When the melting was completed, the glass liquids were cast into stainless steel plates. The obtained glass sample was cooled to room temperature at a rate of 10°C/h, and then was cut and polished carefully in order to meet the requirements for optical measurements.

The upconversion luminescence spectra were obtained with a TRIAX550 spectrofluorimeter upon excitation of 980 nm LD with a maximum power of 2 W. In order to compare the luminescence intensity of Er^{3+} in different samples as accurate as we can, the position and power (100 mW) of the pumping beam and the width (1 mm) of the slit to collect the luminescence singnal were fixed under the same condition, and the samples was set at the same place in the experimental setup. In addition, the integrated intensities for the green and red emissions were also calculated to illustrate the variations of the luminescence intensity. All the measurements made were taken at room temperature.

3. Results and discussion

Fig. 1 shows the room temperature upconversion emission spectrum in the range of 500–700 nm for Er^{3+}/Yb^{3+}-codoped TPC10 and TPC50 glasses under 980 nm excitation. Three intense emission bands centered at 530, 545, and 658 nm corresponding to the transitions $^4S_{3/2}\rightarrow{}^4I_{15/2}$, $^2H_{11/2}\rightarrow{}^4I_{15/2}$ and $^4F_{9/2}\rightarrow{}^4I_{15/2}$, respectively, were simultaneously observed. It can be seen that the upconversion luminescence intensities for green (530 and 545 nm) and red (658 nm) emissions of Er^{3+} in TPC50 glass are a lot larger than those in TPC10 glass. It is also important to point out that the green emission is bright enough to be observed by the naked eye at excitation power as low as 50 mW for Er^{3+}/Yb^{3+}-codoped TPC50 glass at room temperature. Fig. 2 shows the dependence of $PbCl_2$ content on upconversion luminescence intensity. With increasing $PbCl_2$ content, the intensities of green (530 nm) emission intensity increases slightly, while the green (545 nm) and red (658 nm) emission intensities increase more than that of green (530 nm) emission.

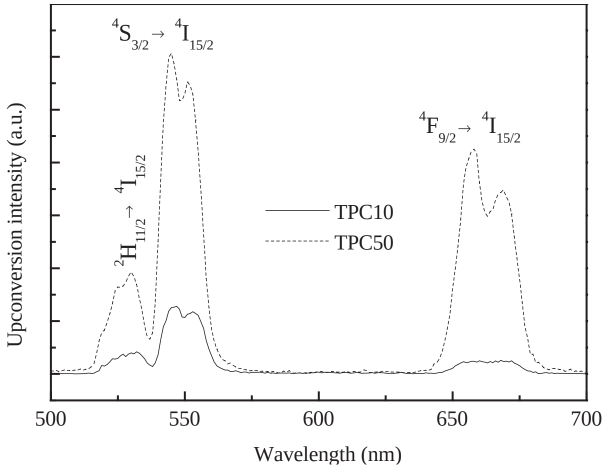

Fig. 1. Upconversion luminescence spectra of Er^{3+}/Yb^{3+}-codoped TPC10 and TPC50 glasses under 980 nm excitation at room temperature.

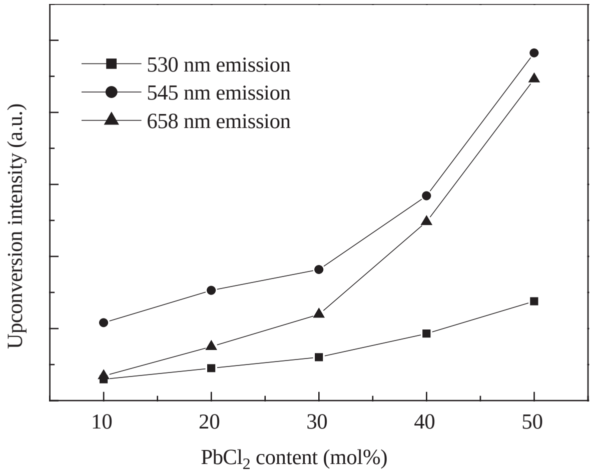

Fig. 2. The dependence of $PbCl_2$ content on upconversion luminescence intensities of Er^{3+}/Yb^{3+}-codoped TPCx ($x = 10, 20, 30, 40, 50$ in mol%) glasses.

In an upconversion mechanism the upconversion emission intensity I_{UP} will be proportional to mth power of the IR excitation intensity I_{IR}, i.e.,

$$I_{UP} \propto I_{IR}^m, \tag{1}$$

where m is the number of IR photons absorbed per visible photon emitted. A plot of $\log I_{UP}$ versus $\log I_{IR}$ yields a straight line with slope m. Fig. 3 shows such a plot for the green (530 and 545 nm) and red (658 nm) emissions, and the values of m obtained are 1.91, 1.96, and 1.90, respectively. The results confirm that a two-photon upconversion process is assigned to the green and red emissions from $^2H_{11/2}$, $^4S_{3/2}$ and $^4F_{9/2}$ levels, respectively [4].

According to the energy matching conditions and the quadratic dependence on 980 nm pump intensity, the upconversion mechanisms in this system under 980 nm excitation are explained as illustrated in Fig. 4 [19–20]. For the green emissions, in the first step, the $^4I_{11/2}$ level is directly excited with 980 nm light by ground state absorption (GSA) and/or by energy transfer (ET) process from $^2F_{5/2}$ level of Yb^{3+}:$^2F_{5/2}(Yb^{3+})+{}^4I_{15/2}(Er^{3+})\rightarrow{}^4I_{11/2}(Er^{3+})+{}^2F_{7/2}(Yb^{3+})$. Since Yb^{3+} has a much larger absorption cross-section than Er^{3+} in the 980 nm region, the ET process is dominant to the excitation of $^4I_{11/2}$ level. The second step involves the excitation processes based on the long-lived $^4I_{11/2}$ level as follows: excited state absorption (ESA) $^4I_{11/2}(Er^{3+})$ + a photon $\rightarrow{}^4F_{7/2}(Er^{3+})$ and ET $^2F_{5/2}(Yb^{3+})+{}^4I_{11/2}(Er^{3+})\rightarrow{}^2F_{7/2}(Yb^{3+})+{}^4F_{7/2}(Er^{3+})$. For an Er^{3+} ion in the $^4F_{7/2}$ excited state the interaction with a nearby Er^{3+} ion in the ground state would lead to two Er^{3+} ions at the $^4I_{11/2}$ level. This process can be represented as follows: $^4F_{7/2}(Er^{3+})+{}^4I_{15/2}(Er^{3+})\rightarrow{}^4I_{11/2}(Er^{3+})+{}^4I_{11/2}(Er^{3+})$. However, the transition probability involved in the above processes can be small, and so the $^4F_{7/2}$ level is populated. The populated Er^{3+} $^4F_{7/2}$ level then relaxes rapidly and non-radiatively to the next lower levels $^2H_{11/2}$ and $^4S_{3/2}$ resulting from the small energy gap between them. The above processes then produces the two $^2H_{11/2}\rightarrow{}^4I_{15/2}$ and $^4S_{3/2}\rightarrow{}^4I_{15/2}$ green emissions centered at 530 and 545 nm, respectively. Since the energy gap below the $^4S_{3/2}$ level is larger, for example, over 3100 cm^{-1} obtained from the absorption spectrum data of Er^{3+}/Yb^{3+}-codoped TPC50 glass, and the non-radiative transition through mutiphonon relaxation from $^4S_{3/2}$ level becomes smaller. Therefore, the bright green upconversion luminescence was emitted through the $^4S_{3/2}\rightarrow{}^4I_{15/2}$ transition. The red emission entered at 658 nm is originated from the $^4F_{9/2}\rightarrow{}^4I_{15/2}$ transition. The population of $^4F_{9/2}$ are based on the processes as follows: ESA: $^4I_{13/2}(Er^{3+})$ + a photon $\rightarrow{}^4F_{9/2}(Er^{3+})$, and CR between Er^{3+} ions: $^4I_{13/2}(Er^{3+})+{}^4I_{11/2}(Er^{3+})\rightarrow{}^4I_{15/2}(Er^{3+})+{}^4F_{9/2}(Er^{3+})$, and ET from Yb^{3+}:$^2F_{5/2}(Yb^{3+})+{}^4I_{13/2}(Er^{3+})\rightarrow{}^2F_{7/2}(Yb^{3+})+{}^4F_{9/2}(Er^{3+})$. The $^4I_{13/2}$ level is populated owing to the non-radiative relaxation from the upper $^4I_{11/2}$ level. Besides, the non-radiative process from $^4S_{3/2}$ level, which is populated by means of the process described previously, to the $^4F_{9/2}$ level also contributes to the red emission.

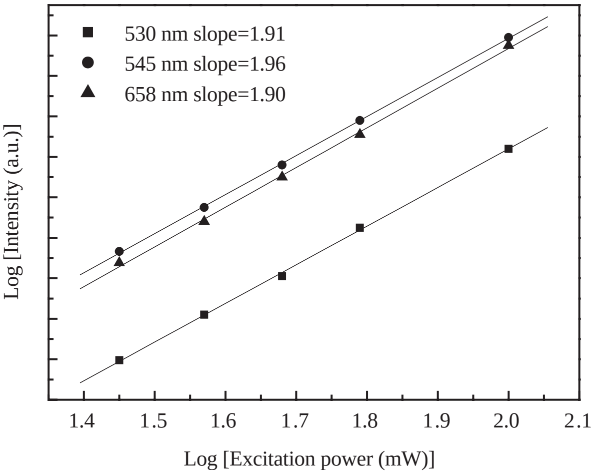

Fig. 3. Dependence of upconversion fluorescence intensity on excitation power under 980 nm excitation for Er^{3+}/Yb^{3+}-codoped TPC50 glass.

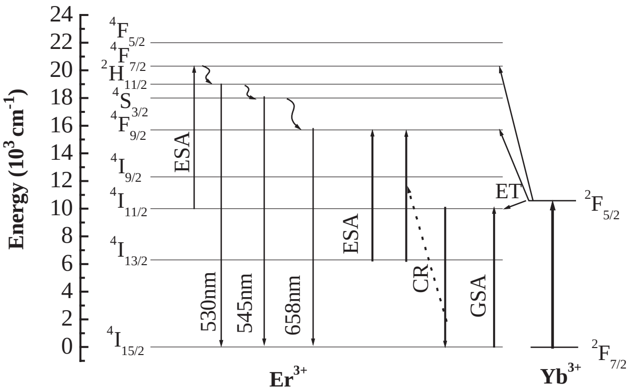

Fig. 4. Energy level diagram of Er^{3+} and Yb^{3+} and upconversion mechanisms of Er^{3+}-doped lead chloride tellurite glasses by 980 nm excitation.

4. Conclusions

We have demonstrated frequency upconversion luminescence of Er^{3+}/Yb^{3+}-codoped lead chloride tellurite glasses under 980 nm excitation. The intense green (530 and 545 nm) and red (658 nm) emissions are observed at room temperature. The upconversion processes involved a sequential two-photon absorption for the green and red emissions. With increasing $PbCl_2$ content, the intensities of green (530 nm) emission intensity increases slightly, while the green (545 nm) and red (658 nm) emission intensities increase more than that of green (530 nm) emission. The intense green uoconversion luminescence of Er^{3+}/Yb^{3+}-codoped TPC50 glass can act as potential materials for developing upconversion optical devices.

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